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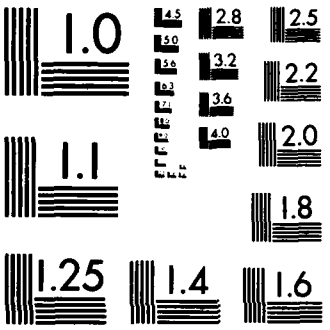

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Large diameter, 1 kg in weight, high purity polycrystalline and (100) oriented InP single crystals can be routinely prepared, with background carrier concentrations of 2-4x10^{15}/cc and room temperature mobilities in excess of 4000cm^2/v-sec.

The large diameter (Approx. 3in.), (100) oriented undoped single crystals have unusually low dislocation densities. Sulfur doped crystals are practically dislocation free.

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N00014-82-C-2372
Final Report
September 1983

DEVELOPMENT OF HIGH PURITY InP CRYSTALS

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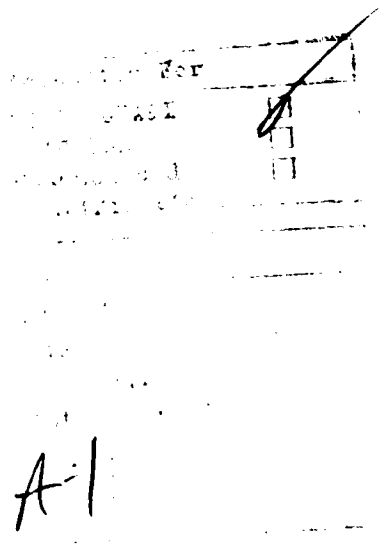
I. INTRODUCTION

InP is becoming an important semiconductor for a wide variety of optoelectronic and microwave applications. This diversity of device requirements imposes strict demands on the properties of the InP substrate, particularly on material purtiy and defect density. This program addressed both of these factors. Initially, we examined the electrical properties of polycrystalline InP synthesized by the injection of Phosphorous to B_2O_3 encapsulated In, and the dependence of such properties of In, P, and B_2O_3 procured commercially. Subsequently, starting material that yielded the highest purity polycrystalline charges was exclusively used in the growth of undoped and Fe doped crystals oriented along the (100) direction.



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II. DISCUSSION

A. Polycrystalline Growth

One of the primary goals of this program was to investigate the effect of the source of the starting materials on the electrical properties of the synthesized polycrystalline InP. The polycrystalline material was prepared by the injection of Phosphorous to B_2O_3 encapsulated In in the high pressure crystal puller under an N_2 overpressure of approximately 600 psi.. Initially it was proposed that the raw materials would be evaluated based on the electrical properties of single crystal grains obtained from crucible shaped charges weighing 600gm. It was decided, however, at the beginning of this program to increase the size of the polycrystalline charge to 1100gm since it did not require any ampoule or heater modifications. Figure 1 shows such a charge having a diameter of 80mm. Electrical evaluation was done by Van der Pauwe measurements at 300°K and 77°K. Since the polycrystalline growth process typically yields large (1-3cc) crystallites, all material evaluation was performed on single crystal wafers extracted from these crystallites.

Table I lists the In, P and B_2O_3 commercial sources that supplied material for this study. All synthesis experiments were performed in SiO_2 crucibles.

Table II shows a summary of the results obtained from the various permutations of the starting materials attempted. It is clear that In from Mitsubishi is of higher purity compared to that purchased from the other two suppliers. With respect to P, both Mitsubishi and Alussuisse supplied materials were comparable in purity

a)

b)

Figure 1: InP, Fully stoichiometric, Crucible shaped polycrystalline charge.
a) Top.
b) Bottom.

TABLE I

MATERIAL		SUPPLIER	GRADE
In:	A	Mitsubishi	6'9
	B	Preussag	6'9
	C	J M C	A'1
P:	A	Mitsubishi	6'9
	B	Alussiuse	6'9
	C	Canyonlands	6'9
B_2O_3:	A	L.G. Williams	
	B	Rasa	H.P.
	C	Rasa	S.H.P.

Table II
Polycrystalline InP Characterization

	1	2	3	4	5	6	7	8	9	10
In Source	A	B	C	A	B	C	A	B	A	A
P Source	A	A	A	A	A	A	B	B	C	A
B_2O_3 Source	A	A	A	B	B	B	B	B	B	C
300°K										
$(N_d-N_a)\times10^{15}$/cc	2.46	4.00	4.20	3.20	4.07	2.20	3.40	3.40	3.89	1.90
μ (cm^2/v-sec)	4480	3500	4020	4520	3910	4190	4230	4190	4140	4870
ρ (Ω-cm)	0.566	0.447	0.37	0.43	0.332	0.654	0.433	0.426	0.387	0.676
77°K										
$(N_d-N_a)\times10^{15}$/cc	2.01	3.04	3.30	2.80	3.39	1.88	2.90	2.80	3.20	1.70
μ (cm^2/v-sec)	25970	15800	18440	33490	27810	25990	33420	25690	24470	38040
ρ (Ω-cm)	0.12	0.13	0.102	0.067	0.066	0.127	0.063	0.087	0.08	0.096

while those supplied by Canyonlands were of slightly lower purity. Finally, the B_2O_3 supplied by L.G. Williams was clearly of lower and inconsistent quality. The material, however, supplied by Rasa was superior. Close to the end of this phase we were supplied with a sample of super high purity (S.H.P.) B_2O_3 from Rasa. The single result using this material along with In and P supplied by Mitsubishi yielded the highest purity and lowest compensation polycrystalline InP obtained.

A further attempt was made to improve the background carrier concentration of the polycrystalline InP by pretreating the In prior to P injection. One run was made with In that was heated under rather low vacuum (50-100μ) at 1000°C for one hour in the high pressure puller. Subsequently, the charge was cooled to room temperature, the puller was opened, and the P ampoule was attached to the seed holder. One 125gm of S.H.P. grade B_2O_3 from Rasa was placed on top of the In, and the synthesis proceeded in the normal manner.

Electrical evaluation of single crystal grains from the polycrystalline material indicate:

	300°K	77°K
(N_D-N_A)/cc	4.37×10^{15}	3.68×10^{15}
Mobility (cm^2/v-sec)	4100	26490
Resistivity (Ω-cm)	0.349	0.061

These results are inferior to those obtained with material from the same batches without the In vacuum baking.

B. Single Crystal Growth

Once the materials sources that produce the lowest background carrier concentration polycrystalline InP were identified, they were used exclusively for the growth of undoped and Fe doped single crystals. The goal of this effort was to determine the lowest Fe concentration required to yield InP single crystals (100) oriented, having resistivities greater than $10^6 \Omega$-cm.

Charges 7 and 10 (see Table II)--Polycrystalline Run #s 1176 and 1179--were used for the first series of experiments. These two charges had background carrier concentrations of $2\text{-}3 \times 10^{15}$/cc and mobilities at 77°K greater than 33000 cm^2/v-sec.

Charge 7 was divided into two equal parts of approximately 500gms each. Two single crystal runs, numbers 2240 and 2241, were made using B grade Super High Purity (SHP) B_2O_3 supplied by Rasa Industries, and Fe (Johnson Matthey 5'9 grade) having concentration in the liquid of 0.005 and 0.01 $^w/_o$. Both of these crystals were grown along the (100) direction; Both were badly twinned; And both were non-insulating.

It should be pointed out that the above single crystals were grown with B_2O_3 from a new batch compared with that used in the growth of polycrystalline charge #10. Although the source purity and moisture content as specified by the manufacturer were the same, we encountered serious difficulties in using this particular batch of B_2O_3--not concerning the purity, but the visibility through the B_2O_3 during growth. To a great extent this darkening was reponsible for the severe twinning observed.

The highest purity polycrystalline charge, #1179, was divided into three equal parts. Approximately 330gms was provided to NRL,

330 gms were used for the growth of an undoped (100) oriented single crystal which was delivered to NRL and 330gms were used for the growth of a (100) oriented Fe doped crystal with Fe concentration in the melt of 0.015 $^{W}/_{o}$. The Fe used was in wire form and was supplied by NRL. Evaluation wafers from this crystal were supplied to NRL.

The polycrystalline material supplied to NRL was used to grow a (111) oriented undoped InP single crystal having the following electrical properties:

		300°K	77°K
Top:	$(N_D-N_A)/cc$	$4.93x10^{15}$	$4.22x10^{15}$
	Mobility (cm^2/v-sec)	4255	28,163
	Resistivity (Ω-cm)	0.298	.053
Bottom:	$(N_D-N_A)/cc$	$7.32x10^{15}$	$5.94x10^{15}$
	Mobility (cm^2/v-sec)	4544	26,121
	Resistivity (Ω-cm)	.185	.045

This represents the highest purity single crystal obtained at any time using polycrystalline starting material synthesized by the injection of P to B_2O_3 encapsulated In at the stoichiometric point.

It has been noted repeatedly that growth of (100) oriented InP single crystals is plagued by severe twinning problems attributed to a number of reasons, including moisture content in the B_2O_3. We have observed that bubbles that get attached to the solid-liquid interface normally initiate defects in the form of high dislocation stacking faults and twin formation. Since our polycrystalline charges weigh approximately 1100gms we designed a new 150mm hot zone for the growth of 3" in diameter, (100) oriented InP single crystals. To date we have made numerous runs with very encouraging results.

Figure 2 shows a (100) oriented InP, Fe doped single crystal weighing 1.0 kg and having a diameter of 2.8". The defect density of these large diameter crystals is unusually low. Figure 3 shows a plot of the defect density of an undoped InP wafer from a (100) grown InP single crystal weighing 1 kg. The defects were delineated with the Huber etch at room temperature. It should be pointed out that such crystals when doped to levels greater than $6x10^{18}$/cc with sulfur are practically dislocation free.

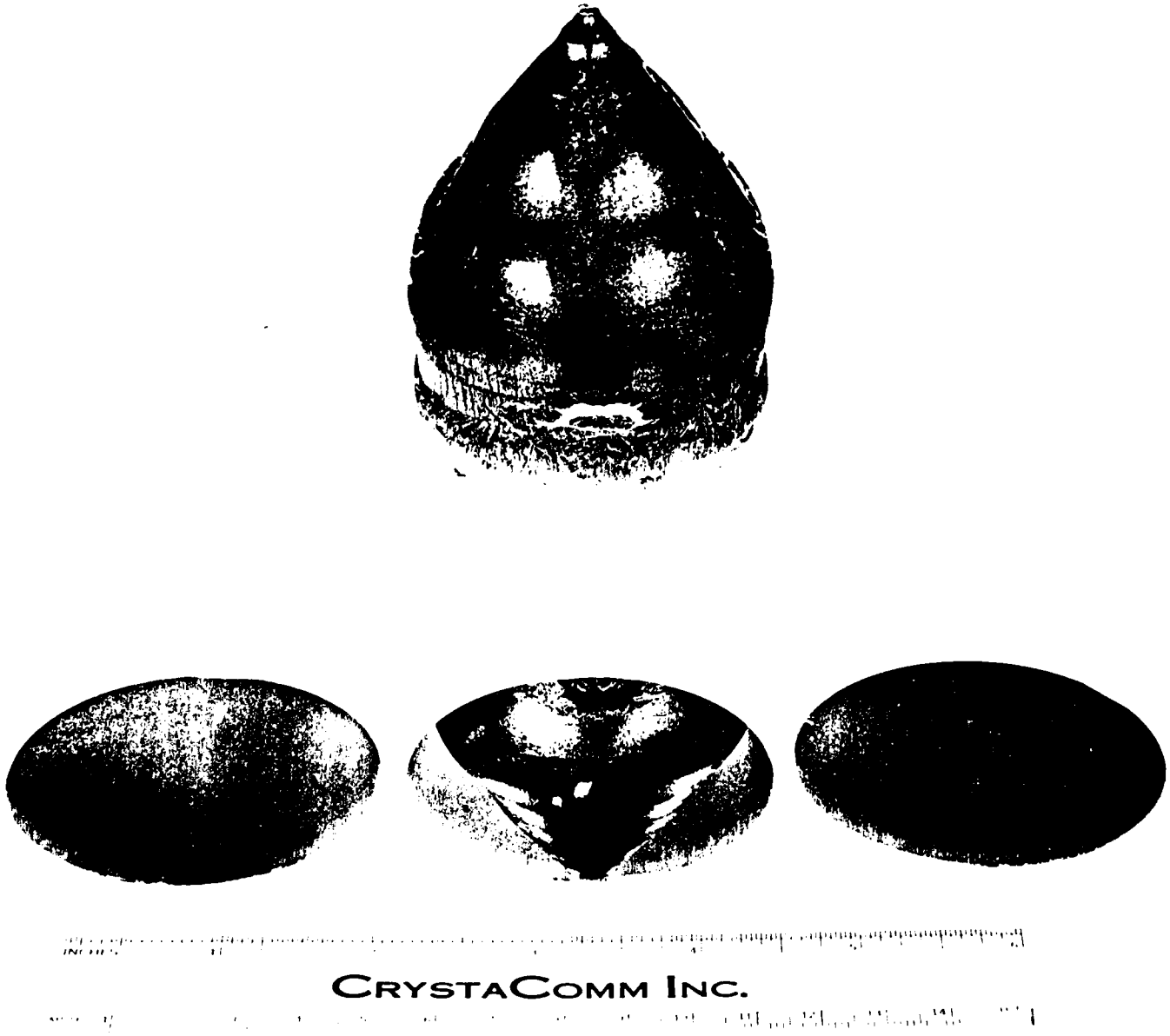

Figure 2: Fe doped InP (100) grown, twin-free, 2.8" diameter, 1 kg single crystal.

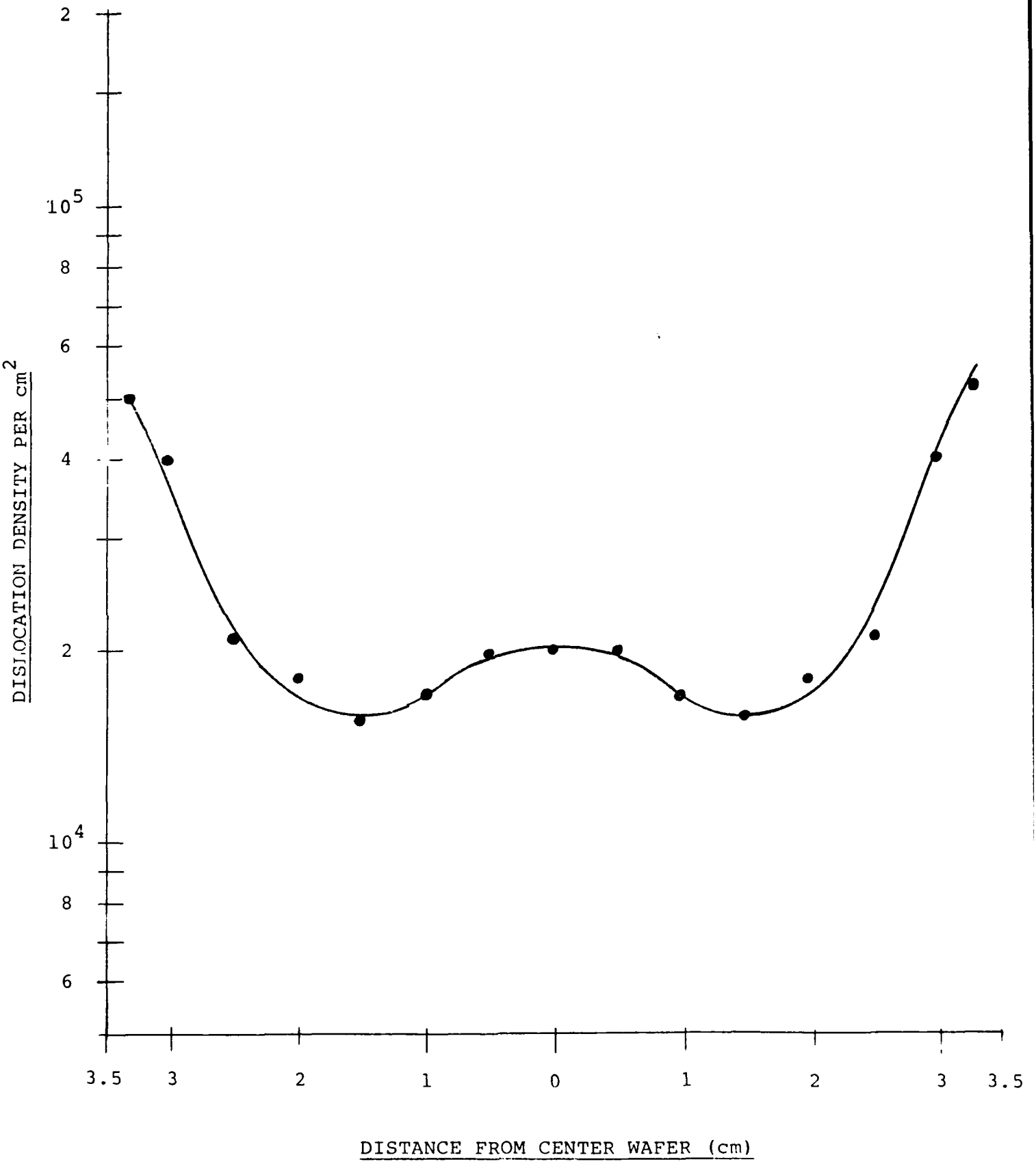

Figure 3: Radial distribution of dislocation density in an undoped (100) grown, 70mm diameter, InP, twin-free single crystal.

SUMMARY

Under this program we evaluated commercial supplies of In, P and B_2O_3 and the relationship of the starting material source on the purity of polycrystalline, fully stoichiometric, crucible-shaped InP charges synthesized by the injection of P to B_2O_3 encapsulated In. The background carrier concentration of such charges was in the $2\text{-}4\text{x}10^{15}$/cc range, with carrier mobilities at 77°K in excess of 38,000 cm^2/v-sec.

Undoped single crystals grown from such charges had background carrier concentrations of $4.9\text{x}10^{15}$/cc and 77°K mobilities of 26121 cm^2/v-sec. The growth of Fe doped (100) oriented single crystals requires an Fe concentration of 0.15 weight per cent in order to yield material with resistivities in the low 10^6 Ω-cm range at the top of the crystal.

A new resistance-heated hot zone has been developed that makes possible the growth of 3 inch, low defect density, (100) oriented InP single crystals.

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